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(54) **Ink composition**

(57) An ink composition comprises a colouring agent dissolved or dispersed in a fluid carrier medium, and is characterised in that:

a. the fluid carrier medium is provided at least in part by one or more polymerisable monomers which are capable of being polymerised under the action of actinic radiation; and

b. the colouring agent is initially translucent to the actinic radiation, but undergoes a change upon exposure of the composition to the actinic radiation to form a coloured form of the colouring agent.

A method for forming images comprises applying the ink composition to a substrate and curing it with actinic radiation, notably by exposure to UV light.

**GB 2 318 356 A**

TITLE: COMPOSITION AND METHOD

5 The present invention relates to a composition and to a method for using that composition, notably to an ink composition which is curable under ultra violet radiation and to a method for using that ink.

BACKGROUND TO THE INVENTION:

10 Inks for use in an ink jet printer are predominantly formulated as solvent based or water based compositions containing a dye or pigment in a fluid carrier together with a film forming resin which provides a solid matrix containing the dye or pigment when the ink droplets dry  
15 after they have been printed. These compositions must meet stringent viscosity and other requirements in order that they should be capable of being ejected as discrete droplets through the nozzle of the printer or of being formed into uniformly sized and spaced apart droplets by  
20 the application of pressure or vibration pulses to a jet of the ink. The need to use low viscosity inks results in compositions which contain low amounts of non-volatile materials resulting in poor mechanical and chemical resistance properties.

25 Whilst ink jet technology has developed to the point at which a wide range of ink formulations can be made for a wide range of uses, problems arise in that solvents introduce health and safety hazards and water based  
30 formulations present problems for use on non-porous surfaces and have a comparatively long drying time.

In order to overcome these problems, alternative fluid carriers for the dye or pigment have been proposed. For  
35 example, fusible carriers have been used in the so called

hot melt ink compositions. However, this requires the use of controlled heating of the ink and the print head through which the molten ink flows to prevent over heating or solidification due to cooling of the ink within the ink flow system. This adds complexity and cost to the construction and operation of an ink jet printer and the printed image is often susceptible to softening at temperatures close to ambient.

It has also been proposed, in for example European Patent Application No 0465039 A1, to formulate a conductive ink using a non-volatile polymerisable monomer to provide the fluid carrier medium. After application to a substrate, the ink is cured by causing polymerisation of the monomer to form a solid polymer by exposing the ink to ultra violet radiation. The use of a non-volatile monomer is claimed to reduce the need for the presence of a solvent hitherto considered necessary in polymerisable ink compositions containing partially polymerised carriers to achieve the low viscosity required for use in an ink jet printer. Furthermore, the ability to use up to 100% non-volatile material as the carrier in such compositions enables high density images with good physical properties to be achieved. However, problems are encountered in achieving rapid curing of such polymerisable monomer compositions, notably with a black dye or pigment, due to absorption of the actinic radiation by the dye or pigment. Such absorption of the curing radiation may also lead to degradation of the dyestuff and other ingredients in the ink composition. In order to reduce the susceptibility of the composition to delayed curing due to absorption of the actinic radiation, it has been proposed to increase the proportion of di-, tri-, tetra- or other partial polymers in the monomer carrier, since these are more rapidly cured upon exposure to actinic radiation.

However, such higher partial polymers are usually more viscous than the corresponding monomer and their use gives unacceptably high viscosity compositions. It has also been proposed to overcome the problem of absorption by the use of selected different dyes or pigments which combine to provide the desired colour but which allow UV radiation at selected discrete wavelengths to pass.

We have now devised an ink formulation which can be cured by exposure to UV or other actinic radiation without the need to use selected and discrete wavelengths for the radiation, thus permitting readily available wide band width energy sources to be used to cure a wide range of ink compositions.

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides an ink composition comprising a colouring agent dissolved or dispersed in a fluid carrier medium, characterised in that:

- a. the fluid carrier medium is provided at least in part by one or more polymerisable monomers which are capable of being polymerised under the action of actinic radiation; and
- b. the colouring agent is initially translucent to the actinic radiation, but undergoes a change upon exposure of the composition to the actinic radiation to form a coloured form of the colouring agent.

The composition preferably also contains one or more polymerisation initiators, notably free radical photo-initiators.

By using a colouring agent which is initially translucent

to the actinic radiation, substantially the full energy of the radiation can penetrate the film of the fluid carrier laid down by the printer so that initiation of the polymerisation of the monomer is more rapid and complete than where a coloured dyestuff or pigment is used which absorbs the radiation and can prevent polymerisation taking place in an acceptable time. The use of such a translucent colouring agent also enables radiation of a broad wavelength band width to be used, since it is no longer necessary to match the wavelength of the radiation to the materials being used so as to minimise absorption as required in prior proposals. Moreover, since the amount of the applied radiation which is lost through absorption is reduced, it is possible to achieve satisfactory curing of the ink composition using a lower energy source of the actinic radiation than hitherto.

The polymerisable monomer for present use can be selected from a wide range of UV curable materials. The invention can be applied to inks for use in a wide range of printing processes. However, it is of especial application with ink jet printers. The monomer, therefore, preferably has an initial viscosity of less than 25 Cps at 25°C so as to be suitable for use in a wide range of conventional ink jet printers. For convenience, the invention will be described hereinafter in terms of ink compositions for use with ink jet printers.

Typically, the monomer will contain ethylenic unsaturation to provide the reactive groupings at which polymerisation takes place. Thus, preferred monomers for present use are acrylic or methacrylic acids or esters thereof. The nature of the ester group will also affect the speed of polymerisation and the hardness of the solid polymer produced. The optimum ester grouping can be determined

by simple tests. However, we prefer to use esters containing a cyclo-aliphatic moiety, for example based upon a five, six, seven or eight membered ring carrying one or more saturated or unsaturated alkyl substituents.

5 Thus, suitable monomers for present use include octyl acrylate, decyl acrylate, glycidyl methacrylate, N-vinyl pyrrolidone, phenoxyethyl acrylate, nonylphenol ethoxylate acrylate, ethyleneglycolmethacrylate, isobornyl acrylate, ethylhexyl acrylate, 2-hydroxyethyl methacrylate, 10 oxyethylated phenol acrylate, lauryl acrylate, butanediol monoacrylate, b-carboxyethyl acrylate, isobutyl acrylate, polypropylene glycol monomethacrylate and mixtures thereof. In general we have found that the use of cycloaliphatic esters of acrylic acid, notably isobornyl 15 acrylate, provide a satisfactory balance between speed of cure and the hardness of the printed droplet.

If desired, mixtures of monomers may be used to produce solid co-polymers.

20 It may be desirable to incorporate one or more polyfunctional polymerisable monomers and/or oligomers, since we have found that the presence of such polyfunctional materials aids rapid curing of the liquid carrier and also affects the properties, for example the 25 chemical stability, hardness and brittleness, of the cured polymer. Such polyfunctional monomers include di-, tri- or tetra-functional polymerisable monomers, for example 1,6-hexanediol di-(meth)acrylate, tetraethylene glycol 30 diacrylate, tripropylene glycol diacrylate, butanediol diacrylate, polyethylene glycol diacrylates, ethoxylated trimethylolpropane triacrylate and mixtures thereof. It is usually preferred that the polymerisable materials for present use contain a total of from 90 to 100% by weight 35 of the monofunctional and difunctional monomers, and up

to 20% by weight of the tri- or tetrafunctional monomers and, for convenience, the term polymerisable monomers will be used herein to include such mixtures of mono- and poly-functional monomers.

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The polymerisable monomers will usually provide all the fluid carrier for the other components of the ink. However, if desired, the compositions may contain up to 10% by weight of a suitable organic solvent or co-solvent for the polymerisable monomers.

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The monomers undergo polymerisation upon exposure to UV radiation. However, it will usually be desired to incorporate one or more polymerisation photo-initiators in the composition. Such initiators include, for example 2,2-dimethoxy-1,2-diphenylethan-1-on; 2-hydroxy-2-methyl-1-phenyl-propan-1-one; benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one; 1-hydroxy-cyclohexyl-phenyl ketone; and mixtures thereof. The polymerisation initiator can be present in an amount of up to 10% by weight of the polymerisable monomer in the ink composition and the optimum amount can be determined by simple test.

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The colour forming component in the ink composition of the invention is a material which is initially substantially translucent to the UV radiation but which undergoes a change in its form upon exposure of the composition to UV radiation to generate a coloured image which is less translucent to the radiation. Thus, the colouring agent can be one which itself undergoes a change upon exposure to the actinic radiation to convert from a translucent form to a coloured or opaque form, for example by the loss of hydroxyl groups from a base form of a C I Basic dyestuff. Alternatively, the ink composition can contain a material which generates a component upon exposure to

actinic radiation which component interacts with the colouring agent to convert the colouring agent to its coloured or opaque form, for example by the generation of hydrogen ions from an aromatic hydroxy compound which is sensitive to actinic radiation, the hydrogen ions then interacting with hydroxyl groups carried, for example, by the base form of the C I Basic dyestuff to develop a coloured form of the dyestuff.

Preferably, the colour forming component is a dyestuff which is soluble in the polymerisable monomer. Suitable dyestuffs include C I Basic dyes in the carbonium base form of the dye. Such base forms exhibit low absorbency in the UV and/or visual light spectrum, but undergo transformation to revert to the coloured Colour Index Basic form of the dye upon exposure to UV light. Typical of the C I Basic dyes which form carbonium base forms are Basic Orange 2 (base form Solvent Orange 3), Basic Violet 2 (base form Solvent Violet 8), Basic Blue 8 (base form Solvent Blue 2), Basic Blue 26 (base form Solvent Blue 4) and Basic Violet 10 (base form Solvent Red 49). The carbonium base forms of such dyestuffs can readily be produced by treating commercially available C I Basic dyes with an organic or inorganic alkali or base and extracting excess alkali or base from such a treated dye by water washing. The alkali treated C I Basic dyes are often available commercially, for example from BASF under the Trade Mark Neptun, and can be used in the present invention after extraction of excess alkali.

The colour forming component is typically present in from 0.1 to 3% by weight of the ink composition.

As indicated above, the coloured form of the dye may be formed upon exposure to actinic radiation. However, it



will often be desirable to incorporate one or more materials which release hydrogen ions upon exposure to actinic radiation so as to provide a source of hydrogen ions in the composition which aid conversion of the base form of the dye to the coloured Basic form. Such materials include aromatic hydroxy compounds such as phenols or naphthols. Such materials are used in sufficient amount to provide at least the stoichiometric amount of hydrogen ions to cause conversion of the base form to the coloured form. It will usually be preferred to use an excess of from 10 to 100% of that stoichiometric amount. The optimum amount will depend upon the nature of the material, the nature of the dyestuff and the radiation which is used to cure the composition and can readily be determined by simple trial.

The ink composition may contain other ingredients to enhance its properties for use in an ink jet printer. Thus, where the ink is to be used in a so called continuous jet ink jet printer, the ink desirably contains sufficient of an ionic material to render the ink conductive so that it can accept a charge. Typical salts which can be incorporated in the ink include ammonium, organic base or alkali-metal salts of organic acids, for example ammonium and/or potassium thiocyanates and lithium nitrate.

The compositions of the invention are made by mixing together the necessary ingredients using any suitable technique, for example stirring.

The ink compositions of the invention have physical properties similar to conventional solvent or water based inks and can be applied to a wide range of substrates using conventional ink jet printers. The substrate can

be a porous or non-porous material, for example paper, glass or metal. In some cases, the monomer may interact with a plastic substrate to enhance the adhesion of the printed image to the substrate.

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The printed images are cured by exposing them to actinic radiation. The actinic radiation is preferably provided by UV light, notably UV-A, B or C at wavelengths in the region of from 200 to 500 nm. As stated above, a commercially available source of such UV light, for example an H-type high pressure mercury vapour lamp, can be used which emits a broad band width of radiation and it is not necessary to use a narrow band width UV light source. Preferably, the light source emits UV light at a power of from 20 to 150 watt/cm and the beam of such UV light can either illuminate the whole of the image which is printed, or can illuminate only a portion of the image. In the latter case it will be necessary for the illumination to traverse the whole of the printed image to achieve curing of the polymerisable monomer throughout the printed image. Thus, the substrate carrying the printed image can travel past a stationary source of the illumination, or the source of the illumination can traverse the area of the substrate to which the printed image has been supplied. If desired, a plurality of UV light sources can be used to achieve the illumination of the whole of the printed image.

The invention will be illustrated in the following Examples, in which all parts and percentages are given by weight unless stated otherwise.

Example 1:

An ink composition was prepared by mixing together 85 parts of isobornyl acrylate monomer (IBOA), 5 parts of

ethoxylated trimethylolmethane (ETMP) as a trifunctional monomer to assist curing of the composition, and 10 parts of 2-hydroxy-2-methyl-1-phenyl-propan-1-one as the free radical polymerisation photoinitiator to provide a colourless, clear fluid carrier medium having a viscosity of 9 Cps at 25°C.

The dyestuff C I Basic Violet 2 was treated with aqueous sodium hydroxide to convert the dyestuff into its base form. The base form was extracted with water to remove excess alkali and 5 parts of the base form of the dye were mixed with 98.5 parts of the carrier medium prepared above to give a blue tinged ink composition.

The ink composition was printed through the nozzle of a drop on demand ink jet printer to form a series of images on a range of plastic, glass and metal sheet substrates. The printed images were well defined, but clear and thus not readily perceived.

The printed substrates were passed under a mercury vapour lamp operating at 100 Watt/cm and 300 to 450nm wavelength to give a total exposure time to the UV radiation of 0.5 seconds. This UV radiation caused the printed image to cure and form hard droplet images with an intense blue colour. The colour tended to develop in intensity upon standing for some 30 to 60 minutes after exposure to the UV light. Satisfactory results were achieved when the droplets were allowed to mature for 10 minutes after exposure to the UV light. The matured droplets adhered well to the various substrates and did not crack or drop off the substrate when the substrate was flexed repeatedly.

By way of comparison, when the dyestuff was incorporated

into the fluid carrier medium in its coloured Basic form, curing of the ink was markedly inhibited and hard droplets were not achieved even after 10 minutes exposure to the UV light.

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Example 2.

The process of Example 1 was repeated, except that 1.5 parts of the base form of the dye were mixed with 95 parts of the carrier medium and 2.5 parts of naphtha-2-ol, which releases hydrogen ions upon exposure to UV radiation. An intense blue colour developed immediately after exposure to the UV radiation and the droplets had the same physical properties as in Example 1.

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Example 3.

The process of Example 2 was repeated using a number of different dyes in an amount of 1.2% of the ink composition. The results of these tests were as follows:

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With a 1:1 mixture of the dyes Solvent Orange 3 and Solvent Red 49, the initial ink composition had a viscosity of 12 Cps and a slight pink colour. After exposure to the UV radiation for 0.5 seconds, the printed droplets were hard and had a deep red colour.

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With Solvent Red 49 dye, the cured droplets were bright pink after 0.2 seconds exposure to the UV radiation.

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With Solvent Blue 2 dye, the ink composition had a viscosity of 10 Cps and an initial slightly blue colour. After exposure for 0.5 seconds to the UV radiation, the droplets were hard and had a navy blue colour.

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5 With a 1:1 mixture of Solvent Orange 3 and Solvent Blue 4 dyes, the ink composition had a viscosity of 11 Cps and an initial slightly green colour. After exposure for 0.5 seconds to the UV radiation, the droplets were hard and had a bright green colour.

10 With a 1:1 mixture of Solvent Orange 3 and Solvent Blue 2 dyes, the ink composition had a viscosity of 11 and an initial slightly green colour. After exposure for 0.5 seconds to the UV radiation, the droplets were hard and bright black.

15 By way of comparison, when Basic Violet 10 dye was used, the ink composition had a viscosity of 11 and an initial dark red colour. Although the droplets cured to give hard droplets after 1 second exposure to the UV radiation, the droplets had lost all colour. When Basic Blue 8 dye was used, the initial ink was dark blue but failed to cure, even after 10 minutes exposure to the UV radiation.

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#### Example 4.

25 The process of Example 1 was repeated except that 2,2-dimethoxy-1,2-diphenylethan-1-one was used as the polymerisation initiator. The initial ink had a viscosity of 14 Cps and satisfactory cured droplets as in Example 1 were produced after 1 second exposure to the UV radiation.

#### Example 5.

30 The process of Example 4 was repeated except that the carrier medium contained 90 parts of the monomer, 5 parts of the trifunctional oligomer and 5 parts of the polymerisation initiator to give a colourless ink composition having a viscosity of 13 Cps. The cured droplets after 1 second exposure to the UV radiation were

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as in Example 1.

Example 6.

5 The process of Example 5 was repeated except that the amount of trifunctional oligomer was raised to 10 parts. Satisfactory printed droplets were achieved after less than 0.1 seconds exposure to the UV radiation. However, the viscosity of the ink composition was 52 Cps.

10 Example 7.

The process of Example 5 was repeated except that the monomer and polyfunctional oligomer were as set out below. The cured droplets had good water resistance and very good hardness. The mixtures tested were:

15 IBOA alone or in 1:1 admixture with N-vinyl pyrrolidone and the oligomer was glycerol triacrylate; and  
20 Glycidyl methacrylate as the sole monomer with ethoxylated trimethylolpropane trimethacrylate (ETMPTA) as the oligomer.

Curing within from 1 to 5 seconds was achieved using a mercury vapour lamp operating at 20 Watt/cm.

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CLAIMS:

1. An ink composition comprising a colouring agent dissolved or dispersed in a fluid carrier medium, characterised in that:
- 5           a. the fluid carrier medium is provided at least in part by one or more polymerisable monomers which are capable of being polymerised under the action of actinic radiation; and
- 10           b. the colouring agent is initially translucent to the actinic radiation, but undergoes a change upon exposure of the composition to the actinic radiation to form a coloured form of the colouring agent.
- 15   2. The composition of claim 1, characterised in that it also contains one or more polymerisation initiators.
- 20   3. The composition of claim 2, characterised in that the polymerisation initiator is a free radical photoinitiator.
4. A composition as claimed in any one of the preceding claims, characterised in that the polymerisable monomer is a cycloaliphatic ester of an acrylic acid.
- 25   5. A composition as claimed in any one of the preceding claims, characterised in that the composition also contains one or more polyfunctional polymerisable monomers and/or oligomers.
- 30   6. A composition as claimed in any one of the preceding claims, characterised in that the polymerisable materials comprise from 80 to 100% by weight of monofunctional or difunctional monomers and up to 20% by weight of tri- or tetrafunctional monomers.

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7. A composition as claimed in any one of the preceding claims, wherein the colouring agent is a base form of a CI Basic dyestuff.

5 8. A composition as claimed in claim 7, characterised in that the basic dyestuff is a carbonium base form of the dyestuff.

10 9. A composition as claimed in either of claims 7 or 8, characterised in that the composition also contains an aromatic hydroxy compound which releases hydrogen ions upon exposure to actinic radiation to assist conversion of the base form of the dyestuff to the coloured form of the dyestuff.

15 10. A composition as claimed in claim 1, substantially as hereinbefore described with respect to and as shown in the Examples.

20 11. A method for forming a coloured image on a substrate, which method comprises applying a composition as claimed in any one of claims 1 to 10 and exposing the composition to actinic radiation.

25 12. A method as claimed in claim 11, characterised in that the actinic radiation is UV radiation at wavelengths in the range 200 to 500nm.

30 13. A method as claimed in either of claims 11 or 12, characterised in that the radiation is emitted at a power of from 20 to 150 watt/cm.

35 14. A method as claimed in any one of claims 11 to 13, characterised in that the ink composition is applied by means of an ink jet printer.





Application No: GB 9621533.0  
Claims searched: 1-14

Examiner: K. Macdonald  
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**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C3V(VAE,VBC)

Int CI (Ed.6): C09D

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
Y	EP 0465039 A1 (DOMINO) see column 2, lines 14-21	1 and 11 at least
Y	WO 89/05464 A1 (PPG) see Claim 1; page 12, lines 25-27	1 and 11 at least
Y	WO 88/00223 A1 (PLESSEY) see page 1, lines 1-5; Example 1	1 and 11 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.